AN EXPERIMENTALIST'S GUIDE TO ROTATIONAL CONSTANTS WITH LOW-COST THEORY

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Microwave spectroscopy is a widely applied tool for determining molecular structures, studying molecular astrophysics, and in more recent times decomposing complex mixtures. All of these applications are made possible due to the tight connection between the observable rotational transitions and a molecule's rotational constants, which in turn depend on its principal moments of inertia. Electronic structure calculations are often used to provide predictions of rotational constants, although much like other molecular properties, the accuracy depends heavily on the method and basis used. Accurate estimates based on "proper" quantum chemistry require highly correlated methods such as coupled-cluster theory, along with large basis sets that incorporate effects such as core-valence electron correlation and scalar relativity. For larger molecules, this approach remains intractable due to the excessive computational cost, thus empirical scaling of low-cost theoretical constants is highly desirable. In this talk, we will present a large systematic benchmark study comprising 11 commonly used low-cost electronic structure theories, 7 basis sets, and 78 closed-shell species of varying elemental composition. By comparing with experimentally determined values, our analysis ranks the performance of each method/basis combinations in our set, highlighting the best combinations and revealing potential shortcomings and weaknesses of select methods. Finally, we determine empirical scaling constants for each method/basis combination that can be used to account for the effect zero-point vibration on equilibrium rotational constants.